

[DESCRIPTION]

FIELD OF THE INVENTION

The present invention relates to a negative-working heat-sensitive material which is suitable for making a lithographic printing plate by direct-to-plate recording and to a method for imaging said heat-mode recording material by means of an infrared laser.

BACKGROUND OF THE INVENTION

Lithographic printing is the process of printing from specially prepared surfaces, which contain a lithographic image consisting of areas that are capable of accepting ink (oleophilic areas), and areas that do not accept ink but are water-accepting (hydrophilic areas). In so-called wet lithographic printing methods, both water or an aqueous dampening liquid (also called fountain solution) and ink are applied to the plate surface that contains the hydrophilic and oleophilic areas. The hydrophilic areas are soaked with water or the dampening liquid and are thereby rendered lithophilic.

Various heat-mode plate materials are known which can be used as a lithographic master for printing with greasy inks. Ablative plates are the best known examples of so-called processless plates, i.e., plates which do not require any processing, and therefore can be used as a printing plate immediately after exposure. The heat, which is generated in the recording layer of such ablative plates by light absorption of a laser beam, removes a hydrophilic or oleophilic topcoat to expose an underlying, hydrophilic, respectively hydrophobic surface, thereby defining the necessary differentiation of ink-accepting areas between the printing and non-printing regions.

For example, DE-A-2 448 325 discloses a lithographic printing plate comprising a base plate, a light-absorbing layer provided with a polyimide coating, a topcoat of a polymer having a different melting temperature than the base plate, and a layer of a heat-sensitive polymer. An image printing plate of this

plated which can be used in an inkjet printer. The printing material is processed. The plate is called a "light sensitive printing plate" or "recording plate" for direct exposure. It is also called a "direct negative printing plate". A film mask is required and held over the plate. The recording material that have been exposed to the laser are rendered ink-absorbing and define the image areas i.e. the printing areas.

Other disclosures in **DE-A-2 448 325** concern "direct negative" printing plates comprising e.g. hydrophilic aluminum foil or coated with a water-soluble laser light-absorbing addm. absorbing dye or with a coating based on a mixture of hydrophilic polymer and laser light-absorbing dye (Arg. 1-42mm). Further examples of heat-mode recording materials for preparing "direct negative" printing plates have been described in e.g. **DE-A-2 607 207**, **DD-A-213 530**,

DD-A-217 645 and **DD-A-217 914**. These documents disclose heat-mode recording materials that contain an anodized aluminum support and a hydrophilic recording layer provided thereon. Laser exposure renders the exposed areas insoluble and ink-absorptive, whereas the non-exposed areas remain hydrophilic and water-soluble. Such plates can also be used directly in the press without processing, because the non-exposed areas are removed by the dampening liquid during printing, thereby revealing the anodized aluminum support.

DD-A-155 407 discloses a "classless heat-mode direct negative" printing plate where a hydrophilic aluminum oxide layer is rendered oleophilic by direct laser heat-mode imaging.

The above heat-mode "direct negative" lithographic printing plates are characterized by a low ϵ -value, space and the obtained plates are of poor quality and irreliability.

EP-A-580 393 discloses an "inkjet lithographic printing plate directly imitable by laser lithography" the plate comprising a porous first layer and a second layer underlying the first layer wherein the first layer is characterized by sufficient absorption of infrared radiation and the first and second layers exhibit different affinities to at least one printing liquid.

EP-A-683 728 discloses a "heat-mode direct negative" printing plate comprising a porous hydrophilic support and a hydrophobic layer provided with an ink-absorbing layer, and an "inkjet" printing plate comprising a porous hydrophilic support and a hydrophobic layer provided with an ink-absorbing layer.

US 4,034,183 describes a processless printing plate that comprises a light-absorbing hydrophilic layer coated on a support which is capable of a latent image being formed and cured from an ink repellent to an ink receptive state. All of the examples and teachings require a high power laser and the run lengths of the resulting lithographic plates are limited.

US 3,832,948 describes both a printing plate with a hydrophilic layer that may be ablated by scanning light from a hydrophobic support and also a printing plate with a hydrophobic layer that may be ablated from a hydrophilic support. However, no examples are given.

US 3,964,389 describes a processless printing plate based on the principle of laser transfer of material. This process is very sensitive to transfer defects and requires an additional donor sheet.

US 4,054,094 describes a process of making a lithographic printing plate by using a laser beam to etch away a thin top coating of polysilicic acid on a polyester base, thereby rendering the exposed areas receptive to ink. No details of run length or print quality are given, but it is expected that an uncrosslinked polymer such as polysilicic acid will wear off rapidly and give a short run length.

US 4,081,572 describes a method for preparing a printing master on a substrate by coating the substrate with a hydrophilic polyamic acid and then image-wise converting the polyamic acid to melanophillic polyimide with heat from a flash lamp or a laser. No details of run length, image quality or ink water balance are given.

Japanese Kokai No. 55/105560 describes a method of preparing a lithographic printing plate by laser treatment of a hydrophilic layer coated on a melanophillic support in which the hydrophilic layer contains cellulose with a cellulose alumina, a poly xylene amide or a salt of a carboxylic acid, and a polyacrylic acid and a cellulose ester or a cellulose ether with a hydroxyl group. The cellulose is soluble in the organic solvents of the laser beam.

WO 92/09934 describes a printing plate having a support with a hydrophilic layer and a hydrophobic layer which is partially soluble in an organic solvent.

and 4,4-dimethyl-2-methoxybiphenyl carboxylate. There was also added a polyisobutylene glycol ether containing 10 mol-% of hydroxyl groups. However, such a polyether unit is not suitable for use in a differentiator, because it is not soluble in the developer solution.

All the examples mentioned in the prior art fail to provide a processless direct imagable printing plate which has a high sensitivity, good starting behavior and gives a high resolution.

My disclosed EP-A no. 99202109, filed on 29.06.99, describes a negative-working heat-sensitive material for making lithographic plates comprising an base layer given a hydrophilic character in a hydrophilic surface, an imaging layer and a hydrophobic upper layer. The heat generated during exposure in the imaging layer removes the hydrophilic upper layer by ablation. However, the water-receptance of the un-exposed areas is insufficient and, as a result, the plate has an inferior start-up behavior, i.e. the un-exposed areas take certain unusual adhesions (a defect known as "towing") while printing the first 10 to 50 copies, which are lost due to bad print quality.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a processless material that is suitable for direct heat-sensitive plate recording and is characterized by a high lithographic quality, especially with regard to start-up behavior. This object is realized by the material defined in claim 1. Preferred embodiments are defined in the dependent claims.

DETAILED DESCRIPTION OF THE INVENTION

The lithographic printing plate of the present invention is improved in the order given: a lithographic base layer, a polyisobutylene glycol ether containing polyether unit, a hydrophilic hydrophobic upper layer.

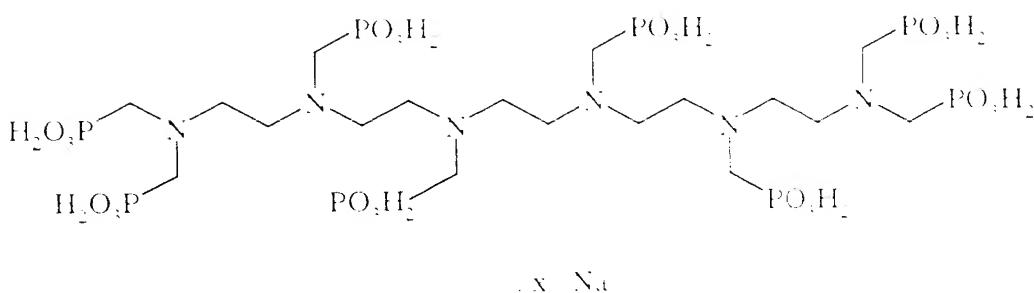
The base layer is heat-sensitive and is characterized by a high sensitivity, good starting behavior and a high resolution. The polyether unit may be a polyether containing hydroxyl groups.

Hydrophilic layers of triallyl-*n*-butylsilyl siloxane, polyvinylacetate hydrolyzed to an extent of at least 50% by weight hardened with a tetraalkyl orthosilicate, e.g., tetraethyl orthosilicate or tetramethyl orthosilicate, as disclosed in e.g., US 3,476,937, are particularly preferred because their use in the present heat-mode recording material results in excellent lithographic printing capabilities.

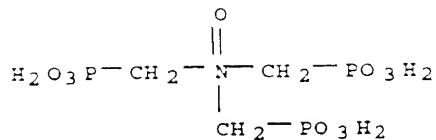
A further suitable or co-linkable polyimide layer is disclosed in EP-A- 514 990. The layer itself is in this embodiment a polyimide film having the following properties: it is a polyimide containing amine or amide functions having at least one free hydroxyl end, amide, imidic, hydroxyl and alkoxylic.



For the first two years of the experiment, the data were collected at the same time each day. The first year the data were collected at 10:00 a.m. and the second year at 10:30 a.m. The data were collected at the same time each day to reduce the effect of the time of day on the data. The data were collected at the same time each day to reduce the effect of the time of day on the data.

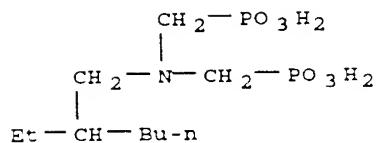


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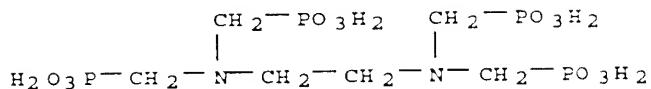
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Brückensubstanz:



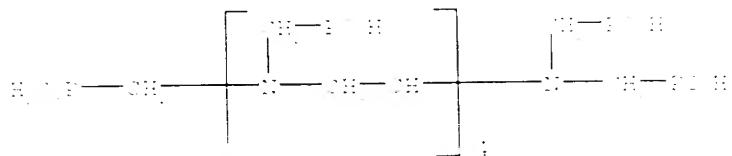
• x Na

Brückensubstanz:

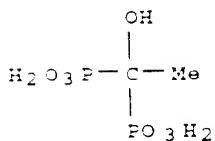


• 4 NH₃

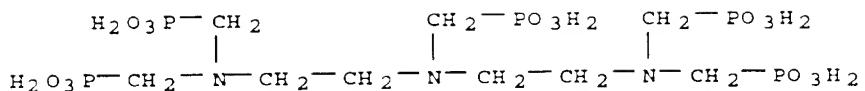
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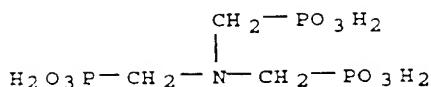


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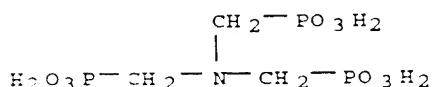


• x Na

Briquet 201-50A :

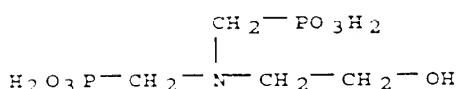


Briquet 201-50 AM :



• x Na

Briquet 541 :



• x Na

Il est possible d'ajouter dans le mélange de sucre et de sucre de canne, de la glycérine et de l'eau pour faire un sirop. Cela facilitera la dissolution de la poudre dans l'eau.

The cross-linked hydrophilic polymer may be obtained by irradiation with electron beam or ultraviolet light or by heating in the presence of a suitable initiator. The cross-linked hydrophilic polymer may be used as a dispersing agent and as a thickening agent in the same manner as the uncross-linked polymer. Particular examples of useful cross-linked hydrophilic polymers may be used in accordance with the present invention are described in EP-A- 601 240, GB-P- 1 419 512, FR-P- 2 300 354, US-P- 3 971 660, and US-P- 4 284 705.

The cross-linked hydrophilic polymer may be obtained by heating the dispersible polymer in the presence of a suitable initiator.

Suitable dispersible polymer for use in the present invention may be particularly irradiated or heated in the presence of a suitable initiator in the wavelength range of the light source used in the cross-linking exposure. Particularly useful types of irradiation are gamma rays and in particular infrared rays as disclosed in EP-A- 908 307 and references and in particular infrared polymer may be carbon black, metal carbides, borides, nitrides, carbides and nitrides and the like, structured oxides. It is also possible to use combinations of polymer dispersion such as; polyvinylidene pyridine, or; polyphenol-based conductive polymer dispersion, carbon black, or graphite, polyimide and the like.

The binder of the dispersible polymer may be particularly selected from the group consisting of polyurethane, polyesters, polyurethanes, polyesters, polyvinyl acetate, or copolymers, particularly those formed by copolymerization of one or more of the binders. It is particularly preferred to use a polyurethane, polyimide, or polyvinyl acetate as the binder, which may be dissolved in GB-P-1 316 398 and DE-A- 2 512 038; and which contains polyisocyanate, polyisocyanate, polyurethane, polyimide, polyvinyl acetate, or the like, and which is dispersible. Also, a structure of an emulsion of a dispersible polymer may be used as the binder, as described by the following.

The cross-linked hydrophilic polymer may be obtained by heating the dispersible polymer in the presence of a suitable initiator. The cross-linked hydrophilic polymer may be used as a dispersing agent and as a thickening agent in the same manner as the uncross-linked polymer. Particular examples of useful cross-linked hydrophilic polymers may be used in accordance with the present invention are described in EP-A- 601 240, GB-P- 1 419 512, FR-P- 2 300 354, US-P- 3 971 660, and US-P- 4 284 705.

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is shown in Figure 10. The total thickness of the photoresist layer is 1.5 micrometers. The air gap is 0.5 micrometers. April 1970.

The dry running weight of the photoresist layer is about 1.6 micrometers between 1.4 and 1.8 micrometers. The thickness of the exposed areas is 1.1 and 1.3 micrometers. If the hydrophilic organic layer is less than 0.11 micrometers, the hydrophilicity of the exp. surf. areas is low due to the underlying lithographic base and the resolution is mainly limited by the exposed areas. If the IR-sensitive hydrophilic layer is too thick, 0.13 micrometers, the effect of the hydrophilic surface on the lithographic base is lost and the resolution may be limited by the non-exposed areas due to toning.

According to the present invention, the lithographic base may be an anodized aluminum support. A particularly preferred lithographic base is an electrolytically pre-treated and anodized aluminum support. The anodized aluminum support may be treated to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicized by treating its surface with a sodium silicate solution at elevated temperature, e.g., 85°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further oxidize the anodized aluminum. Further, the aluminum oxide surface may be rinsed with a sulfuric acid solution until it is clean. This treatment may be carried out at a temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a 10% aqueous solution of acetyl acetone. An aluminum oxide surface may be treated with a hydrophilic alkyl ester of polyvinylbenzyl-polyvinylbenzyl and polyvinylbenzyl-sulfuric acid ester, sulfonic acid esters of polyvinylbenzyl and acetate of polyvinylbenzyl formed by reaction with a substituted alkylbenzyl aldehyde. It is further believed that the various of these treatments may be carried out alone or in combination. More detailed description of these treatments can be found in GB-A- 1 084 070 DE-A- 4 423 140, DE-A- 4 417 907, EP-A- 659 909 EP-A- 537 633 DE-A- 4 001 466, EP-A- 292 801 EP-A- 291 760 and US-P- 4 458 005.

It is believed that the present invention will be of great value in the manufacture of integrated circuit devices, and the like, and that the invention will find wide application.

which is provided with a hydrophilic base layer, and a second, hydrophobic layer. The film may be applied to a substrate, such as a film of aluminum. The base layer is preferably a hydrophilic base layer, which is a layer obtained from a hydrophilic binder, which is linked with a hardening agent such as formaldehyde, phenol, or epichlorohydrin or a hydrolyzed tetraalkylorthosilicate. The latter is particularly preferred.

The hydrophilic binder for use in the base layer is such a hydrophilic copolymer such as homopolymers and copolymers of vinyl alcohol, acrylamide, methyl acrylate, methyl methacrylate, acrylate, methacrylate, and methyl acrylate, and acryloyl acrylate, hydroxethyl methacrylate, maleic anhydride vinylmethylether copolymers. The hydrophilicity of the copolymer or copolymer mixture used is preferably the same as or higher than the hydrophilicity of polyvinyl acetate hydrolyzed to at least an extent of 50% by weight, preferably 70% by weight.

The amount of hardening agent, in particular tetraalkyl orthosilicate, is preferably at least 1.0 parts per part by weight of hydrophilic binder, more preferably between 1.0 and 5 parts by weight, most preferably between 1 parts and 3 parts by weight.

The hydrophilic base layer may also contain substances that improve the mechanical strength and tensile capacity of the layer. For this purpose colloidal silica may be used. The colloidal silica employed may be in the form of any commercially available water dispersion of colloidal silica, for example, having an average particle size up to 400 nm, or may be added in larger particles, up to 10 times size than the colloidal silica, for example, silica prepared according to United States Patent No. 2,711,111 and International Soc. 1951, 20, 10, 16, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 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1219, 1220, 1221, 1222, 1223, 1224, 1225, 1226, 1227, 1228, 1229, 1220, 1221, 1222, 1223, 1224, 1225, 1226, 1227, 1228, 1229, 1230, 1231, 1232, 1233, 1234, 1235, 1236, 1237, 1238, 1239, 1230, 1231, 1232, 1233, 1234, 1235, 1236, 1237, 1238, 1239, 1240, 1241, 1242, 1243, 1244, 1245, 1246, 1247, 1248, 1249, 1240, 1241, 1242, 1243, 1244, 1245, 1246, 1247, 1248, 1249, 1250, 1251, 1252, 1253, 1254, 1255, 1256, 1257, 1258, 1259, 1250, 1251, 1252, 1253, 1254, 1255, 1256, 1257, 1258, 1259, 1260, 1261, 1262, 1263, 1264, 1265, 1266, 1267, 1268, 1269, 1260, 1261, 1262, 1263, 1264, 1265, 1266, 1267, 1268, 1269, 1270, 1271, 1272, 1273, 1274, 1275, 1276, 1277, 1278, 1279, 1270, 1271, 1272, 1273, 1274, 1275, 1276, 1277, 1278, 1279, 1280, 1281, 1282, 1283, 1284, 1285, 1286, 1287, 1288, 1289, 1280, 1281, 1282, 1283, 1284, 1285, 1286, 1287, 1288, 1289, 1290, 1291, 1292, 1293, 1294, 1295, 1296, 1297, 1298, 1299, 1290, 1291, 1292, 1293, 1294, 1295, 1296, 1297, 1298, 1299, 1300, 1301, 1302, 1303, 1304, 1305, 1306, 1307, 1308, 1309, 1300, 1301, 1302, 1303, 1304, 1305, 1306, 1307, 1308, 1309, 1310, 1311, 1312, 1313, 1314, 1315, 1316, 1317, 1318, 1319, 1310, 1311, 1312, 1313, 1314, 1315, 1316, 1317, 1318, 1319

Particular attention has been paid to the design of the main frame and the rear end, in accordance with the latest available knowledge of aerodynamics. The
EP-A- 601 240 GB-P- 1 419 512 FR-P- 2 300 354 US-P- 3 971 660
and US-P- 4 284 705.

As flexible support of a light graphic have in mind that, with the present embodiment it is particularly preferred to use a plastic film e.g. polyethylene terephthalate film, i.e. polyethylene terephthalate film, cellulose acetate film, i.e. lyocell film, polyimide film, etc. The plastic film support may be partly transparent.

It is particularly preferred to use a film of silicon with the adhesion improving layer, also called substrate layer, also being provided. Particularly suitable adhesion improving layers for use in accordance with the present invention comprise a hydrophilic binder and colloidal silica as disclosed in EP-A- 619 524, EP-A- 620 502 and EP-A- 619 525. Preferably, the amount of silica in the adhesion improving layer is between 300 mg per m² and 750 mg per m². Further, the ratio of silica to hydrophilic binder is preferably more than 1 and the surface area of the colloidal silica is preferably at least 300 m² per gram, more preferably at least 400 m² per gram.

preferably the heat-insulating insulation material can be provided with an additional hydrophilic layer, provided on top of the hydrophilic upper layer disclosed above, which comprises an expandable and elastic hydrophilic material, for example described in EP-A no. 99202110, filed on 29.06.99.

temperature such as freezing or heating the image material, or by a chemical treatment. A photochemical treatment of the image material, for example, with an AF is a typical way of a permanent image fixation. A chemical treatment is normally not regarded as a processing step, but it can be a treatment which prevents the hydrophilic areas from being prints or other contamination which may affect the water-solubility of these areas. By a freezing the remaining solute dust on the plate is removed thereby avoiding contamination of the prints. At the same time the hydrophilic areas are covered with a thin layer of the freezing solution including a better surface protection.

Image-wise exposure material with the present invention is preferably an image-wise scanning exposure including the use of a laser or L.E.D. Preferably lasers are used that operate in the infrared or near-infrared, i.e., wavelength range of 700-1600 nm. Most preferred are laser diodes emitting in the near-infrared with an intensity higher than 0.1 mW/cm².

According to the present invention the plate is then ready for printing without an additional development and can be mounted on the printing press.

According to a further embodiment of the present invention is first mounted on the printing cylinder of the printing press and then image-wise exposed for a part of the image material in the printing image recording device. Subsequently to exposing the image material is ready for printing.

The printing plate of the present invention can also be used in the printing press as a separate image recording plate. In this case the printing plate may be a separate image recording plate usually means of a laser, such as an image recording plate which has to be inserted to the cylinder of the print cylinder to be held on the print cylinder instead of printing a printing plate. The details of sleeves are given in British No. 1,511,148, 1975, 1st Oct.

The following examples illustrate the present invention, but it will be understood that the invention is not limited to the examples given.

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For more information on the 2010 Census, visit 2010.census.gov.

A 0.50 mm thick aluminum foil was prepared by immersing the foil in an aqueous solution containing 5 g/l of a 10% hydrochloric acid and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid, 1 g/l of hydrochloric acid and 5 g/l of aluminum ions at a temperature of 45°C and a current density of 1000 A/m² to form a surface topography with an average center-line roughness R_a of 1.5 μm .

After rinsing with demineralized water the aluminum foil was etched with an aqueous solution containing 10 g/l of sulfuric acid and 0.1 g/l of CrO₃ for 180 seconds and rinsed with demineralized water at 25°C.

The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 100 g/l of sulfuric acid at a temperature of 45 °C, a voltage of about 15 V and a current density of 150 A/m² for 30 min in an anodized aluminum film of 3.00 g/m² of Al₂O₃, then washed with de-mineralized water, post-treated with a solution containing polyvinylchlorophenolic acid and a solution containing aluminum triethyl oxide, and subsequently rinsed with de-mineralized water at 15 °C for 10 min and dried.

For more information on the National Institute of Standards and Technology's work in the area of data security, visit www.nist.gov/itl/cybersecurity.

— 1 —

+ 0.01 g Nitrocellulose Red, 10% w/v in water, and
+ 1.00 g Ethylacetate.

0.10 g Dispersin, 0.001 g Polyacrylic acid, 0.001 g 2,6-diphenyl-4-oxazolidinone, 0.001 g 2,6-diphenyl-4-oxazolidinone, and 0.001 g 2,6-diphenyl-4-oxazolidinone.

0.10 g Dymel solution of the following composition:
+ 0.40 g Dymel 301 aqueous latex from Dymel Systems
+ 1.00 g Ethylacetate.

0.06 g Propylene sulfonic acid + 0.01 g of the following
composition:

+ 0.001 g Propylene sulfonic acid
+ 0.004 g Ethylacetate.

0.01 g Ethylacetate

2.00 g Ethylacetate

Preparation of the cross-linked hydrophilic layer layer

After drying the imaging layer, the hydrophilic layer was coated at a wet coating thickness of 1.0 μ m from a solution having the following composition:

0.10 g 0.005% Sil Dispersion (Kodak 510) from Payerl in
water, stabilized with 0.01% DM-4000, 0.001 g Polyvinyl
alcohol from Wacker; the dispersion contained 0.1 g
polyvinyl alcohol versus Sil, average particle size 0.1
 μ m.

0.10 g 0.005% Polyvinyl acetate (PVA) 1000, TM-5 in
water, ethanol 50/50.

1.0 g Crosslinking agent in water.

The pH of this solution was adjusted to 4.0 with 1.0 M KOH. After coating, the layer was hardened for 12 hours at 100 °C.

Example 2: Coating 2

The crosslinked hydrophilic layer was prepared in the same manner as in Example 1, except that the crosslinking agent was 1.0 g of 0.005% polyvinyl acetate (PVA) 1000, TM-5 in water, ethanol 50/50.

added to the starting solution of the hydrophilic polymer. The materials are given in table 1.

The resulting composition was applied to a 100 mm diameter cylinder (244T PMR 260) of a polyimide substrate and dried in a drybox and a laser writing of the pattern. After drying the pattern was mounted on a Heidelberg ST 500 press with a Dahlgren lamp-inking system using K+E 300 Skinner as ink and Polaromatic as dampening liquid. A compressible blanket was used. Subsequently the press was started by allowing the print cylinder with the drawing material mounted thereon to rotate. The dampener rollers of the press were first dropped on the drawing material, then a supply dampening liquid to the imaging material and after 10 revolutions of the print cylinder, the ink rollers were dropped to supply ink. After 10 further revolutions, the paper supply was started.

The start-up behavior is defined as the number of sheets required before toning-free prints were obtained. The results are summarized in table 1.

Examples 4-7

The materials A, B, C and D were prepared in an identical way as the reference material with the exception that in addition to the hydrophilic layer a part of the polyimide film was replaced by a polymer which contains a sulfonic acid pendant group resulting in a layer composition as shown in table 2. The same imaging and dampening material was the same as used in the examples 1-3.

Examples 8 and 9

The materials E and F were prepared in an identical way as the reference material with the exception that a polymer which contains a sulfonic acid pendant group in the polyimide was added to the polyimide. The hydrophilic layer was added to the polyimide layer in the same way as described in example 1. The same imaging and dampening material was the same as used in the examples 1-3.

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For the two-dimensional case, $\Delta x = 10000 \text{ fm}^{-1}$, $\Delta y = 20000 \text{ fm}^{-1}$, $\Delta z = 30000 \text{ fm}^{-1}$.

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Spectroscopic Data for the Various Layers		Spectroscopic Data for the Various Layers	
Layer	Depth	Layer	Depth
1	0-1000	2	1000-2000
3	2000-3000	4	3000-4000
5	4000-5000	6	5000-6000
7	6000-7000	8	7000-8000
9	8000-9000	10	9000-10000
11	10000-11000	12	11000-12000
13	12000-13000	14	13000-14000
15	14000-15000	16	15000-16000
17	16000-17000	18	17000-18000
19	18000-19000	20	19000-20000
21	20000-21000	22	21000-22000
23	22000-23000	24	23000-24000
25	24000-25000	26	25000-26000
27	26000-27000	28	27000-28000
29	28000-29000	30	29000-30000
31	30000-31000	32	31000-32000
33	32000-33000	34	33000-34000
35	34000-35000	36	35000-36000
37	36000-37000	38	37000-38000
39	38000-39000	40	39000-40000
41	40000-41000	42	41000-42000
43	42000-43000	44	43000-44000
45	44000-45000	46	45000-46000
47	46000-47000	48	47000-48000
49	48000-49000	50	49000-50000
51	50000-51000	52	51000-52000
53	52000-53000	54	53000-54000
55	54000-55000	56	55000-56000
57	56000-57000	58	57000-58000
59	58000-59000	60	59000-60000
61	60000-61000	62	61000-62000
63	62000-63000	64	63000-64000
65	64000-65000	66	65000-66000
67	66000-67000	68	67000-68000
69	68000-69000	70	69000-70000
71	70000-71000	72	71000-72000
73	72000-73000	74	73000-74000
75	74000-75000	76	75000-76000
77	76000-77000	78	77000-78000
79	78000-79000	80	79000-80000
81	80000-81000	82	81000-82000
83	82000-83000	84	83000-84000
85	84000-85000	86	85000-86000
87	86000-87000	88	87000-88000
89	88000-89000	90	89000-90000
91	90000-91000	92	91000-92000
93	92000-93000	94	93000-94000
95	94000-95000	96	95000-96000
97	96000-97000	98	97000-98000
99	98000-99000	100	99000-100000

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the first time in 1990, and the first time in 1991, and the first time in 1992.

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